

# Protonation of *D*-Gluconate and its Complexation with Np(V) in Acidic to Nearly Neutral Solutions

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*Key words:* gluconic acid, neptunium, complexation, stability constant, enthalpy.

## Abstract

Thermodynamic properties of the protonation of *D*-gluconic acid (HG<sub>H</sub>4(aq)) and its complexation with Np(V) have been studied in acidic to nearly neutral solutions at  $t = 25$  °C and  $I = 1$  M NaClO<sub>4</sub> by potentiometry, spectrophotometry and calorimetry. The protonation constant ( $\log K_H$ ) and enthalpy ( $\Delta H_H$ ) of the carboxylate group are determined to be  $(3.30 \pm 0.10)$  and  $-(4.03 \pm 0.07)$  kJ·mol<sup>-1</sup>, respectively. Gluconate forms two Np(V) complexes in nearly neutral solutions. The formation constants and enthalpies of complexation are:  $\log \beta_1 = (1.48 \pm 0.03)$  and  $\Delta H_1 = -(7.42 \pm 0.13)$  kJ·mol<sup>-1</sup> for NpO<sub>2</sub>(GH<sub>4</sub>)(aq),  $\log \beta_2 = (2.14 \pm 0.09)$  and  $\Delta H_2 = -(12.08 \pm 0.45)$  kJ·mol<sup>-1</sup> for NpO<sub>2</sub>(GH<sub>4</sub>)<sub>2</sub><sup>-</sup>. The thermodynamic parameters indicate that gluconic acid, like isosaccharinic acid and other  $\alpha$ -hydroxycarboxylic acids, is a slightly stronger acid and forms stronger complexes with Np(V) than simple monocarboxylic acids.

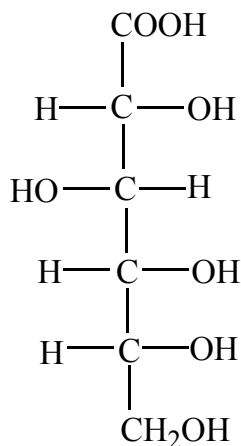
## 1. Introduction

Gluconic acid is one of the organic compounds found in the high-level nuclear wastes at the Hanford site of Washington State, the United States. The presence of gluconic acid in the nuclear wastes could enhance the solubility of actinides and other metal ions by forming soluble complexes, affecting the chemical behavior of actinides in nuclear waste processing. To develop the strategies for treating the nuclear wastes, thermodynamic data on the complexation of gluconate with actinides and lanthanides must be available. Unfortunately, such data are very scarce. There have been a few studies on the complexation of gluconic acid with lanthanides(III) [1-4], Th(IV) [4], U(IV) [5], U(VI) [6] and Am(III) [4]. However, there are no thermodynamic data on the complexation of gluconic acid with neptunium, a major contributor to the total radiation dose of nuclear wastes in a long term. As a result, we have studied in this work the complexation of gluconic acid with Np(V), the most stable valency state of neptunium. Thermodynamic parameters, including the formation constants of Np(V)/gluconate complexes and the enthalpy of complexation, were obtained in nearly neutral solutions ( $pC_H \sim 6$ ) of 1.0 M  $NaClO_4$  at 25°C.

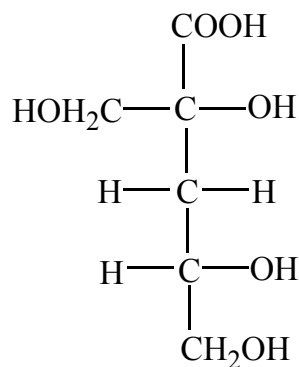
It is known that gluconic acid, like other polyhydroxycarboxylic acids such as isosaccharinic acid, undergoes lactonization in acidic solutions [7-11]. Formation of glucono-lactone is slow and alters the stoichiometric concentrations of gluconic acid and gluconate, thus complicating the determination of the protonation as well as complexation constants with certain techniques. We have conducted detailed thermodynamic/kinetic studies dealing with the lactonization and protonation of gluconic acid in acidic solutions with techniques including ESI-MS (electrospray ionization-mass

spectrometry), NMR and potentiometry [12]. In this paper, we report only the protonation constant determined by potentiometry, taking advantage of the difference in reaction rates between the protonation and lactonization. The main focus of the present work is the determination of the stability constants of gluconate complexes with Np(V). The complexation was studied in nearly neutral solutions ( $pC_H \sim 6$ ). Under these conditions, the stability constants of Np(V) gluconate complexes can be accurately determined because 1) the carboxylate group of gluconic acid is fully deprotonated, 2) glucono-lactone is absent, and 3) the hydrolysis of Np(V) is negligible.

In the paper, gluconic acid refers to *D*-gluconic acid derived from natural *D*-glucose. To be consistent with the notations in the literature, gluconic acid, gluconate and glucono-lactone are denoted by  $HGH_4(aq)$ ,  $GH_4^{-1}$  and  $L(aq)$ , respectively, where the first H refers to the carboxylic acid hydrogen and  $H_4$  refers to the four hydrogens on the secondary alcohols [8,13].



*D*-Gluconic Acid



$\alpha$ -Isosaccharinic Acid

## 2. Experimental

### Chemicals

All chemicals are reagent grade or higher. Distilled and boiled water was used in preparations of all solutions. The stock solution of gluconate was prepared by weighing and dissolving in a volumetric flask an appropriate amount of sodium gluconate purchased from Acros Chemical Company without further purification. The concentration of gluconic acid in the stock solution calculated from the weight was verified by cation exchange and acid-base titration [14].

The Np(V) stock solution in  $\text{HClO}_4$  ( $C_{\text{Np}} \sim 0.1 \text{ M}$ ) was prepared by the procedure in the literature [15]. Solid neptunium dioxide ( $\text{NpO}_2$ ) was dissolved in concentrated HCl under low heating. Concentrated  $\text{HClO}_4$  was added to drive away excess HCl and oxidize neptunium to Np(VI) by fuming. *Caution: Fuming with perchloric acid must be conducted with great care and in the absence of any organic materials. The presence of even the smallest amounts of organic materials may cause an explosion.* Into the pink solution of Np(VI), a small amount of  $\text{NaNO}_2$  was added to reduce Np(VI) to Np(V), resulting in a green solution. The Np(V) was then precipitated as hydroxide with 1 M NaOH. The precipitate was washed three times with water and dissolved with 1 M  $\text{HClO}_4$ . Absorption spectra were collected to confirm that Np(V) was the only oxidation state in the stock solution and determine the concentration of Np(V) ( $\epsilon = 387 \text{ M}^{-1}\text{cm}^{-1}$  at 980.4 nm). Prior to use, working solutions of  $\text{NpO}_2\text{ClO}_4$  were prepared by appropriate dilutions with water and the  $\text{pC}_{\text{H}}$  of working solutions was adjusted to  $\sim 6$  with NaOH. The ionic strength of the working solutions used in potentiometry, spectrophotometry and

calorimetry was adjusted to 1.0 M at 25°C by adding appropriate amounts of sodium perchlorate as the background electrolyte.

### Potentiometry

The potentiometric experiments were carried out at Washington State University (WSU) and Lawrence Berkeley National Laboratory (LBNL) to determine the protonation constant ( $\log K_H$ ) of gluconate. Details of the titration setup have been provided elsewhere [16,17].

A Metrohm pH meter (Model 713) equipped with a Ross combination pH electrode (Orion Model 8102) was used to measure the electromotive force (*EMF*). The original electrode filling solution (3.0 M potassium chloride) was replaced with 1.0 M sodium chloride to avoid clogging of the electrode frit glass septum due to the precipitation of  $KClO_4$ . The *EMF* of the glass electrode in the acidic region can be expressed by Eq. (1).

$$E = E^0 + (RT/F) \ln[H^+] + \lambda_H[H^+] \quad (1)$$

where  $R$  is the gas constant,  $F$  is the Faraday constant and  $T$  is the temperature in K. The last term is the electrode junction potential for the hydrogen ion ( $\Delta E_{j,H^+}$ ), assumed to be proportional to the concentration of the hydrogen ion. Prior to each titration, an acid/base titration with standard perchloric acid and sodium hydroxide was performed to obtain the electrode parameters of  $E^0$  and  $\lambda_H$ . These parameters allowed the calculation of hydrogen ion concentrations from the *EMF*'s in the subsequent titration that immediately followed. Corrections for the electrode junction potential of the hydroxide ion were not necessary in the acidic region. Multiple titrations were conducted with solutions of different

concentrations of gluconate. The protonation constant was calculated with the program Hyperquad [18].

### **Spectrophotometry**

Spectrophotometric titrations were conducted on a Cary-5G UV/Visible/Near IR spectrophotometer (Varian, Inc.) at LBNL to determine the stability constants of the Np(V)/gluconate complexes. A quartz cuvette of 1.0 cm optical length was used and the cuvette holder is maintained at 25°C by a 1×1 peltier system. The absorption spectra of Np(V) in the wavelength range from 950 to 1050 nm were collected as the solution was titrated with gluconate. The stability constants as well as the deconvoluted spectra of the Np(V)/gluconate complexes were calculated with Hyperquad [18].

### **Calorimetry**

Calorimetric titrations were conducted on an isothermal microcalorimeter (Model ITC-4200, Calorimetry Sciences Corp.) at LBNL to determine the enthalpies of the protonation of gluconate and its complexation with Np(V). The performance of the calorimeter was tested by measuring the enthalpy of protonation of tris(hydroxymethyl)-aminomethane (THAM). The measured value was  $-(47.7 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$  at 25°C, compared well with those in the literature [19].

Multiple titrations are carried out for each system. For each titration run,  $n$  experimental values of the total heat produced in the reaction vessel ( $Q_{\text{ex},j}$ ,  $j = 1$  to  $n$ ) were calculated as a function of the volume of the added titrant. These values were corrected for the heat of dilution of the titrant ( $Q_{\text{dil},j}$ ), which was determined in separate runs. The net reaction heat at the  $j$ -th point ( $Q_{\text{r},j}$ ) was obtained from the difference:  $Q_{\text{r},j} = Q_{\text{ex},j} - Q_{\text{dil},j}$ . The values of  $Q_{\text{r},j}$ , in conjunction with the titration conditions and the

constants of protonation and complexation calculated from potentiometry and spectrophotometry, were used to calculate the enthalpies by the computer program MQ90 [20].

### 3. Results and Discussion

#### Protonation of gluconate

The protonation and lactonization of gluconic acid are expressed by equations 2 and 3. The protonation reaction (eq.2) is usually rapid and the equilibrium can be achieved within seconds. On the other hand, literature data [7-10] indicate that lactonization of gluconic acid (eq.3) is negligible in solutions of  $pC_H > 5$  and occurs slowly in solutions of  $pC_H < 5$ . The first-order rate constant of lactonization was determined at 20 – 22°C to be  $3.8 \times 10^{-5} \text{ s}^{-1}$  at  $pC_H$  2.4 [10] and  $1.7 \times 10^{-5} \text{ s}^{-1}$  at  $pC_H$  4.5 [12], corresponding to a reaction time of 7.3 and 16 hrs at  $pC_H$  2.5 and 4.5, respectively. Based on these kinetic data, the maximum extent of lactonization in 30 minutes is estimated to be 5% at  $pC_H$  2.4 and 2% at  $pC_H$  4.5. Taking advantage of the difference in the kinetics between protonation and lactonization, we have conducted relatively fast potentiometric titrations to determine the protonation constant ( $K_H$ ), using a fresh solution of sodium gluconate ( $pC_H \sim 6$ ). Two representative titrations were shown in Figure 1. The titrations were performed with standard  $\text{HClO}_4$  from high  $pC_H$  (6) to low  $pC_H$  (3). The time interval between data points is 60 seconds, sufficient to achieve steady *EMF* readings after each addition, and the titrations were completed within 30 minutes.



Fitting the data shown in Figure 1 by the Hyperquad program results in a value of  $\log K_H = 3.30 \pm 0.01$ , which is in very good agreement with the value obtained by NMR [12]. Taking into consideration of the uncertainty introduced by neglecting the formation of small amounts of lactone in the course of titration, we elect to express the result of  $\log K_H$  from this work as  $3.30 \pm 0.10$  (Table 1). This value indicates that gluconic acid is a slightly stronger acid than simple monocarboxylic acid (e.g.,  $\log K_H \sim 4.6$  for acetic, butanoic and hexanoic acids [21]), but similar to other  $\alpha$ -hydroxycarboxylic acids (e.g.,  $\log K_H \sim 3.6$  for hydroxyacetic, 2-hydroxybutanoic and 2-hydroxyhexanoic acids [21]) and isosaccharinic acid ( $\log K_H \sim 3.2 - 3.3$  [22]). This may suggest the formation of hydrogen bonding between the deprotonated carboxylate group and an adjacent hydroxyl group, which could stabilize the deprotonated form and result in a lower  $\log K_H$ . The presence of such hydrogen bonding has been found for isosaccharinate by recent C-13 NMR data [22].

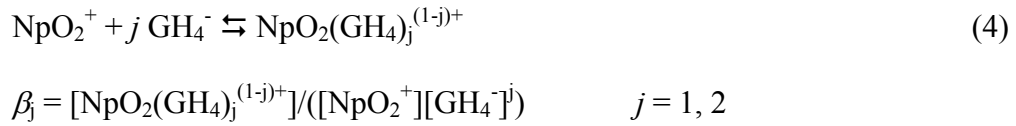
The experimental conditions and the observed reaction heat in the calorimetric titrations are summarized in Table 2. To reduce the uncertainty introduced by lactonization, only the data in the region of  $pC_H > 3.5$  were included in the calculation. The enthalpy of protonation ( $\Delta H_H$ ) was calculated to be  $-(4.03 \pm 0.07) \text{ kJ}\cdot\text{mol}^{-1}$  (Table 1).

The enthalpy of protonation of simple monocarboxylates is usually small and endothermic (e.g.,  $0 \sim 3 \text{ kJ}\cdot\text{mol}^{-1}$  for acetate, butanoate and hexanoate [21]). However, the enthalpy of protonation of  $\alpha$ -hydroxycarboxylates is exothermic (e.g.,  $\sim -2 \text{ kJ}\cdot\text{mol}^{-1}$  for hydroxyacetate [21] and  $-7.9 \text{ kJ}\cdot\text{mol}^{-1}$  for isosaccharinate [23]). The enthalpy of protonation of gluconate is similar to that of  $\alpha$ -hydroxycarboxylates.



### Formation Constants of gluconate complexes with Np(V)

Data of a representative spectrophotometric titration are shown in Figure 2a. Factor analysis [18] by Hyperquad indicated that there were three neptunium species that have significant absorbance in the near IR region. The data were fitted by Hyperquad with the formation of two complex species shown in equation 4.



The calculated formation constants are  $\log \beta_1 = 1.48 \pm 0.03$  and  $\log \beta_2 = 2.14 \pm 0.09$  (Table 1). The calculated absorption spectra of Np(V) species,  $\text{NpO}_2^+$ ,  $\text{NpO}_2(\text{GH}_4)(\text{aq})$  and  $\text{NpO}_2(\text{GH}_4)_2^-$ , are shown in Figure 2b.

### Enthalpy of complexation for the gluconate complexes with Np(V)

The experimental conditions and the values of reaction heat are summarized in Table 2. The reaction heat observed at the  $j$ th addition of the titrant,  $Q_{r,j}$ , is a function of the enthalpy of complexation and the change in speciation after the addition:

$$Q_{r,j} = \sum \Delta n_i \Delta H_i^0 \quad (5)$$

where  $\Delta n_i$  is the change of the amount of the  $i$ th species in moles after the  $j$ th addition while  $\Delta H_i^0$  is the enthalpy of formation of the  $i$ th species. In the calculation of enthalpies of complexation, a quantity,  $\Delta h_{v,M}$ , is defined as  $Q_r/n_M$  and used as the error-carrying variables ( $Q_r$  is the overall reaction heat and  $n_M$  is the number of moles of Np(V) in the

cup). The enthalpies of complexation were calculated to be  $\Delta H_1 = -(7.42 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{NpO}_2(\text{GH}_4)(\text{aq})$  and  $\Delta H_2 = -(12.08 \pm 0.45) \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{NpO}_2(\text{GH}_4)_2^-$  (Table 1). Two calorimetric titrations are represented in Figure 3 as the plot of  $\Delta h_{v,M}$  vs.  $n_{\text{bar}}$ , the average ligand number. Using these values and the formation constants of  $\text{NpO}_2(\text{GH}_4)(\text{aq})$  and  $\text{NpO}_2(\text{GH}_4)_2^-$ , the curves simulating the calorimetric titrations were calculated and are shown to be in excellent agreement with the experimental data in Figure 3. The data of two titrations with different concentrations of Np(V) coincide very well, indicating the absence of polynuclear Np(V) species in the titrations.

### **Log $\beta$ – pK<sub>a</sub> correlation for Np(V) carboxylate complexation**

As a hard acid cation, the interaction of  $\text{NpO}_2^+$  with carboxylate ligands in aqueous solution is expected to be ionic and electrostatic in nature [24]. This means that the stability constants of Np(V) carboxylate complexes may correlate with the protonation constants of the ligands, because the protonation of carboxylates is also predominantly an electrostatic interaction. Figure 4 shows the relationship between the formation constants of the 1:1 Np(V) carboxylate complexes and the pK<sub>a</sub> of the ligand. The data for simple monocarboxylates (acetate, benzoate, chloroacetate and dichloroacetate) show a strong linear correlation. However, the stability constants of the Np(V) complex with gluconate and several  $\alpha$ -hydroxycarboxylates (hydroxyacetate, 2-hydroxypropanoate, 2-hydroxy-2-methylpropanoate) are significantly above the straight line, suggesting that these complexes have “enhanced” stability with respect to the log  $\beta$  – pK<sub>a</sub> correlation. Such enhancement could result from the participation of the  $\alpha$ -hydroxyl group to form a chelate complex with Np(V).

Comparison of enthalpy of complexation between simple carboxylate complexes and polyhydroxycarboxylate complexes could provide further insight into the coordination modes. The complexation of U(VI) with simple carboxylates (e.g., acetate, malonate) is entropy driven and endothermic [17,21,25], resulting from the large energy required for the dehydration of the cation and the anion. However, complexation of U(VI) with isosaccharinic acid, a polyhydroxycarboxylic acid, is slightly exothermic [23], implying that the hydroxyl group participates in the complexation and the participation of a hydroxyl group results in a more favorable enthalpy of complexation. Probably, the hydroxyl group is less hydrated than the carboxylate group so that less energy is required to dehydrate the hydroxyl group than the carboxylate group. The same discussion is applicable to the complexation of gluconic acid, where the exothermic enthalpy implies that the hydroxyl group of gluconic acid plays a role in the complexation, as the enhanced stability of the complexes suggests.

#### **4. Summary**

In acidic solutions, gluconic acid behaves similarly to other monocarboxylic acids, but with a slightly stronger acidity possibly due to the formation of hydrogen bonding between the negatively charged carboxylate group and the  $\alpha$ -hydroxyl group that stabilizes the deprotonated form. Two complexes of gluconate with Np(V),  $\text{NpO}_2(\text{GH}_4)(\text{aq})$  and  $\text{NpO}_2(\text{GH}_4)_2^-$ , have been identified in nearly neutral solutions. The stability constants of the complexes are higher than those expected from a  $\log \beta - \text{p}K_a$  relationship for simple monocarboxylates based on the electrostatic model, suggesting the participation of the  $\alpha$ -hydroxyl group in complexation.

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Table 1. Thermodynamic parameters of the protonation of gluconate and its complexation with Np(V) in acidic to nearly neutral solutions,  $t = 25^\circ\text{C}$ ,  $I = 1.0 \text{ M NaClO}_4$ . The error limits represent  $3\sigma$ . Data for isosaccharinic acid are included for comparison. \*A composite protonation constant ( $\log K_{\text{composite}}$ ) that equals to  $\log [K_{\text{H}}(1 + K_{\text{L}})]$  [23].

Reaction	$\log K_{\text{H}}$ or $\log \beta_{\text{M}}$	$\Delta G^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H^\circ$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\circ$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Reference
$\text{H}^+ + \text{GH}_4^- = \text{HGH}_4(\text{aq})$	$3.30 \pm 0.10$	-18.83	$-(4.03 \pm 0.07)$	$50 \pm 1$	this work
$\text{NpO}_2^+ + \text{GH}_4^- = \text{NpO}_2\text{GH}_4(\text{aq})$	$1.48 \pm 0.03$	-8.45	$-(7.42 \pm 0.13)$	$3.5 \pm 0.4$	
$\text{NpO}_2^+ + 2\text{GH}_4^- = \text{NpO}_2(\text{GH}_4)_2^-$	$2.14 \pm 0.09$	-12.21	$-(12.08 \pm 0.45)$	$0.4 \pm 1.5$	
$\text{H}^+ + \text{isa}^- = \text{Hisa}(\text{aq})$	$3.27 \pm 0.02$				[22]
	$3.65 \pm 0.05^*$	-20.83	$-(7.94 \pm 0.03)$	$43 \pm 1$	[23]
$\text{UO}_2^{2+} + \text{isa}^- = \text{UO}_2\text{isa}^+$	$2.91 \pm 0.15$	-16.61	$-(1.0 \pm 1.0)$	$52 \pm 4$	[23]

Table 2. Stepwise heat of reaction in the calorimetric titrations.  $I = 1.0 \text{ M NaClO}_4$ ,  $t = 25^\circ\text{C}$ . Titration conditions:  $V^0 = 0.900 \text{ mL}$  for all runs;  $C_H/C_L/C_M$  in mM are: Run 1, 1.0e-3/10.0/0; Run 2, 1.0e-3/20.0/0; Run 3, 1.0e-3/0/1.09, Run 4, 1.0e-3/0/1.63. Titrant: 49.3 mM  $\text{HClO}_4$  for Run 1 and 2; 50.0 mM  $\text{NaGH}_4$  for Run 3 and 4.

Protonation of gluconic acid				Complexation of gluconic acid with Np(V)			
Run 1		Run 2		Run 3		Run 4	
$V_{\text{titr.}}, \mu\text{L}$	$Q_r, \text{mJ}$	$V_{\text{titr.}}, \mu\text{L}$	$Q_r, \text{mJ}$	$V_{\text{titr.}}, \mu\text{L}$	$Q_r, \text{mJ}$	$V_{\text{titr.}}, \mu\text{L}$	$Q_r, \text{mJ}$
4.0	0.981	3.6	0.739	5.0	0.5400	5.0	0.7700
9.0	0.946	8.6	0.971	10.0	0.4500	10.0	0.6700
14.0	0.948	13.6	0.968	15.0	0.3950	15.0	0.5698
19.0	0.951	18.6	0.966	20.0	0.3669	20.0	0.5707
24.0	0.947	23.6	0.964	25.0	0.3348	25.0	0.5367
29.0	0.939	28.6	0.964	30.0	0.3171	30.0	0.5036
34.0	0.933	33.6	0.962	35.0	0.2994	35.0	0.4733
39.0	0.928	38.6	0.962	40.0	0.2829	40.0	0.4415
44.0	0.925	43.6	0.961	45.0	0.2637	45.0	0.4104
49.0	0.921	48.6	0.961	50.0	0.2473	50.0	0.3822
54.0	0.917	53.6	0.960	55.0	0.2315	55.0	0.3528
59.0	0.912	58.6	0.957	60.0	0.2126	60.0	0.3205
64.0	0.909	63.6	0.957	65.0	0.1965	65.0	0.3045
69.0	0.895	68.6	0.956	70.0	0.1843	70.0	0.2839
74.0	0.892	73.6	0.952	75.0	0.1686	75.0	0.2621
79.0	0.878	78.6	0.949	80.0	0.1582	80.0	0.2486
84.0	0.873	83.6	0.942	85.0	0.1486	85.0	0.2287
		88.6	0.941	90.0	0.1364	90.0	0.2177
		93.6	0.940	95.0	0.1293	95.0	0.1988
		98.6	0.936	100.0	0.1219	100.0	0.1842
		103.6	0.935	105.0	0.1111	105.0	0.1699
		108.6	0.936	110.0	0.1037	110.0	0.1580
		113.6	0.932	115.0	0.1007	115.0	0.1460
		118.6	0.937	120.0	0.0962	120.0	0.1385
		123.6	0.930	125.0	0.0932	125.0	0.1319
		128.6	0.923	130.0	0.0912	130.0	0.1201
		133.6	0.922	135.0	0.0871	135.0	0.1149
		138.6	0.921	140.0	0.0836	140.0	0.1120
		143.6	0.915	145.0	0.0808	145.0	0.1080
		148.6	0.906	150.0	0.0783	150.0	0.1010
		153.6	0.907	155.0	0.0761	155.0	0.0924
		158.6	0.904	160.0	0.0723	160.0	0.0901
		163.6	0.895	165.0	0.0722	165.0	0.0900
				170.0	0.0704	170.0	0.0882
				175.0	0.0702	175.0	0.0810
				180.0	0.0697	180.0	0.0780
				185.0	0.0690	185.0	0.0760
				190.0	0.0683	190.0	0.0740
				195.0	0.0678	195.0	0.0710
				200.0	0.0666	200.0	0.0705
				205.0	0.0654	205.0	0.0684
				210.0	0.0648	210.0	0.0690
						215.0	0.0700

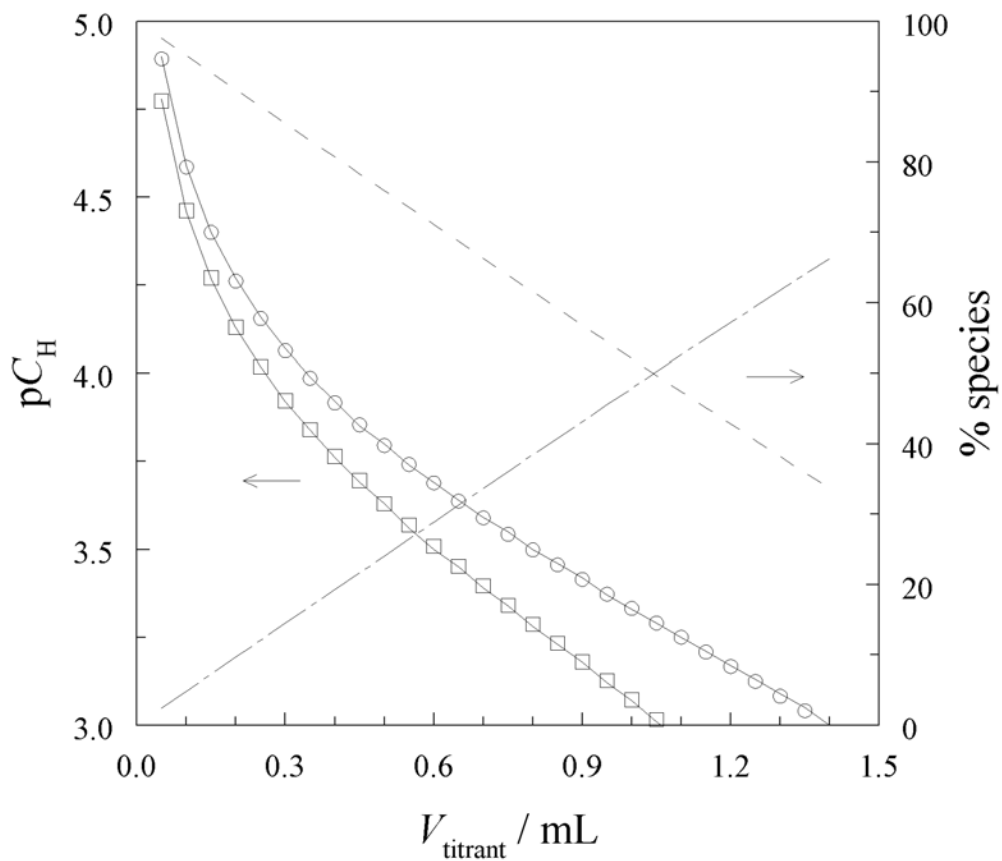


Figure 1. Two potentiometric titrations of the protonation of gluconate,  $t = 25^\circ\text{C}$ ,  $I = 1.0$  M  $\text{NaClO}_4$ . Titrant: 0.9893M  $\text{HClO}_4$ . Cup solutions: Titration I -  $V^0 = 41.00$  mL,  $C_L^0 = 0.02468$  M,  $C_H^0 = 1.0\text{e-}6$  M. Titration II -  $V^0 = 42.00$  mL,  $C_L^0 = 0.04819$  M,  $C_H^0 = 1.0\text{e-}6$  M. Symbols:  $\square$  and  $\circ$  – experimental  $pC_H$  for Titrations I and II. Solid lines – fitted  $pC_H$ . The dash line and dotted-dash line represent the percentages of  $\text{GH}_4^-$  and  $\text{HGH}_4(\text{aq})$  calculated for Titration II.



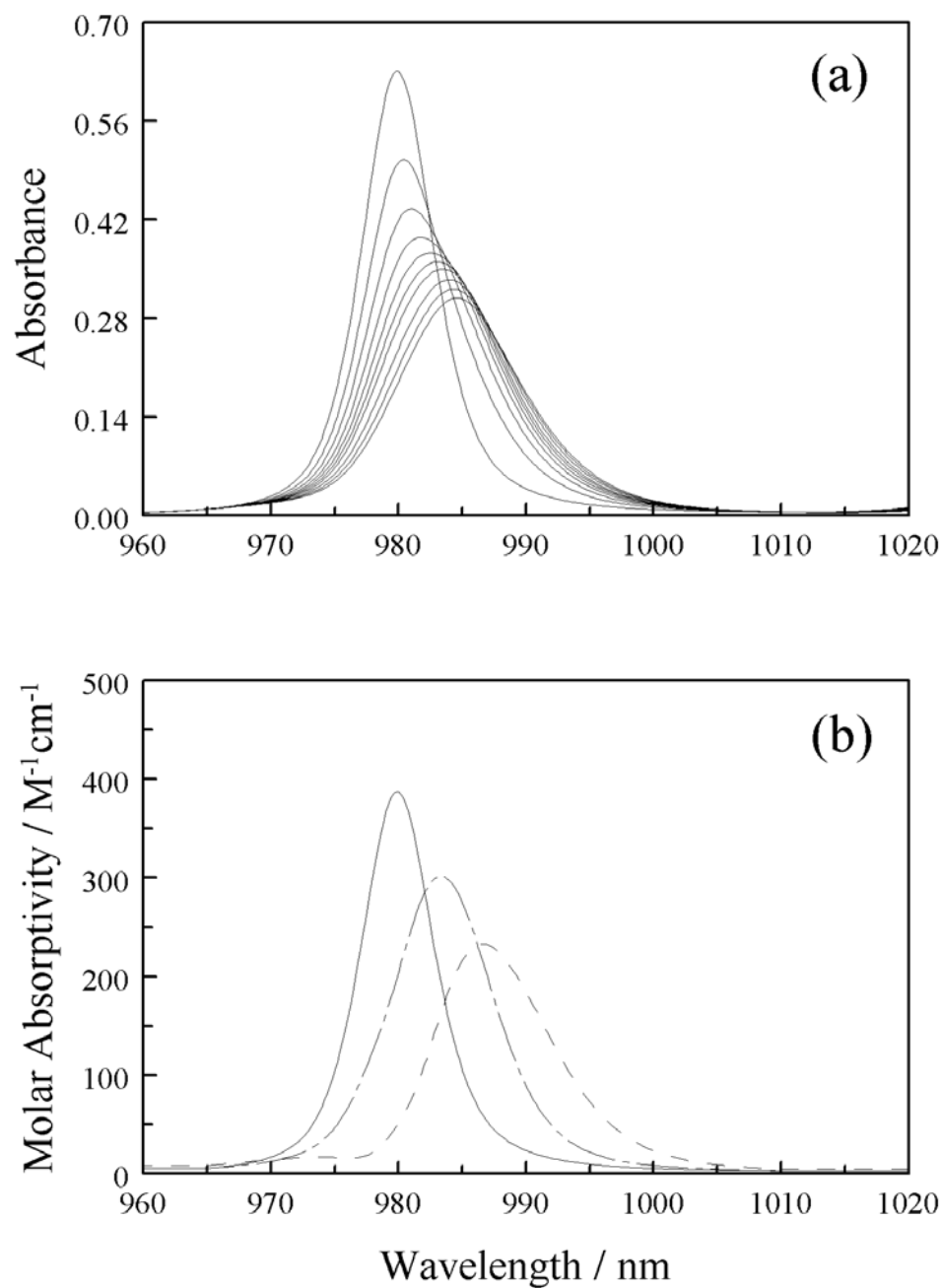


Figure 2. (a) Spectrophotometric titrations of the gluconate complexation with Np(V),  $t = 25^{\circ}\text{C}$ ,  $I = 1.0\text{ M NaClO}_4$ . Cuvette solution:  $C_{\text{Np}}^0 = 0.00163\text{ M}$ ,  $C_{\text{H}}^0 = 1.0\text{e-}6\text{ M}$ ,  $V^0 = 2.5\text{ mL}$ . Titrant:  $1.001\text{ M gluconate}$ ,  $C_{\text{H}}^0 = 1.0\text{e-}6\text{ M}$ . (b) Resolved molar absorptance spectra of Np(V) species in gluconate solution. Solid line:  $\text{NpO}_2^+$ , dotted-dash line:  $\text{NpO}_2\text{GH}_4(\text{aq})$ , dash line:  $\text{NpO}_2(\text{GH}_4)_2^-$ .

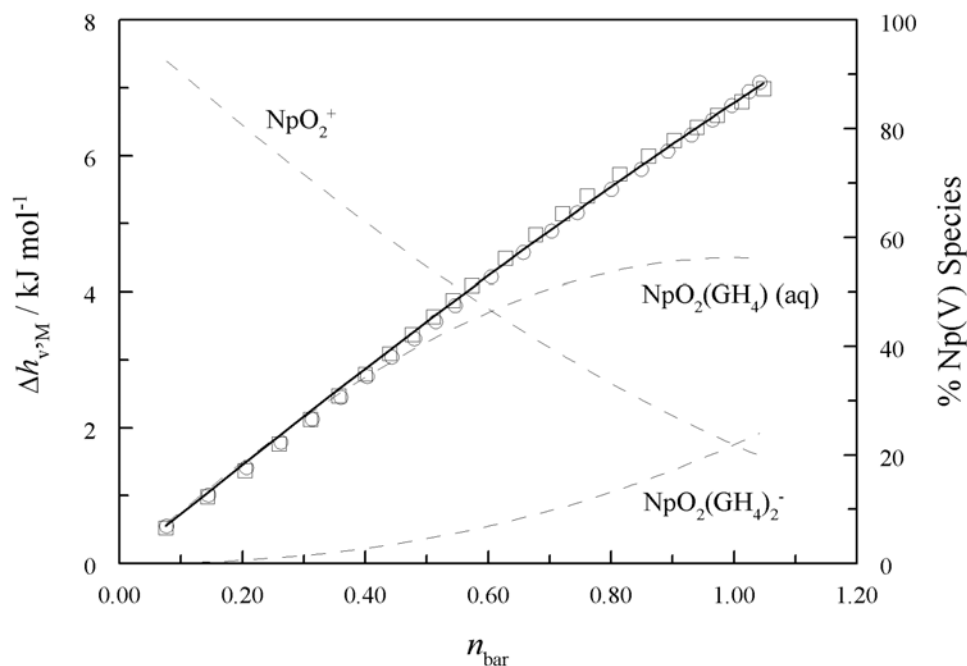


Figure 3.  $\Delta h_{v,M}$  as a function of  $n_{\text{bar}}$ , the average ligand number for the calorimetric titrations of Np(V) gluconate complexation,  $t = 25^\circ\text{C}$ ,  $I = 1.0 \text{ M NaClO}_4$ ,  $V^0 = 0.900 \text{ mL}$ . Titrant:  $0.500 \text{ M}$  gluconate ( $C_H^0 = 1.0\text{e-}6 \text{ M}$ ); cup solution ( $C_H^0 = 1.0\text{e-}6 \text{ M}$ ):  $C_{\text{Np}}^0 = 0.00109 \text{ M}$  (O),  $0.00163 \text{ M}$  ( $\square$ ). Symbols (O/ $\square$ ): experimental data (left y-axis), number of points reduced for clarity; solid line: calculated. Dashed lines: speciation of Np(V) species in the titrations (right y-axis).

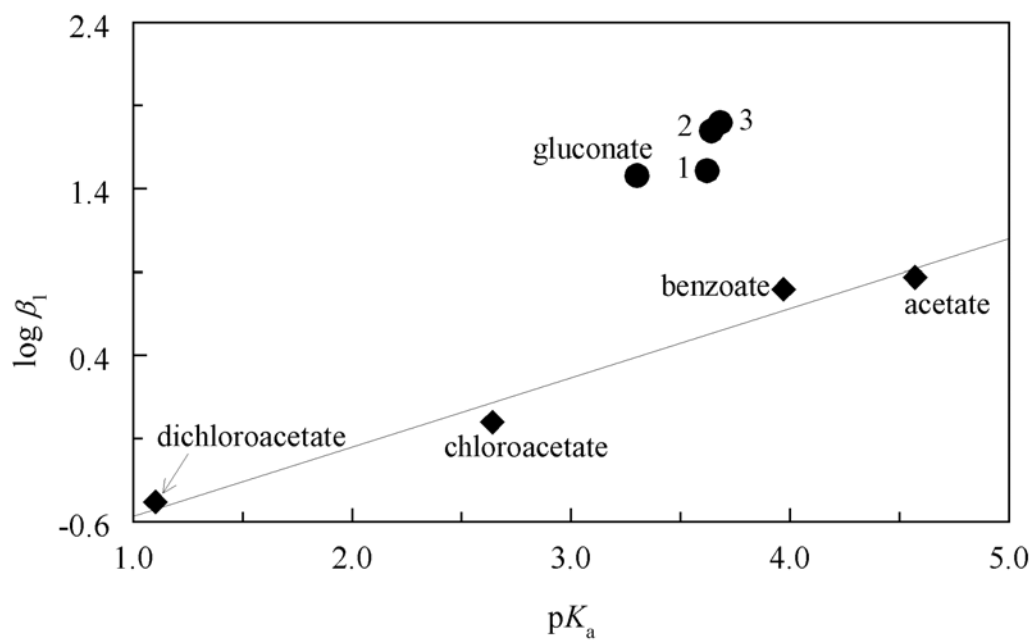


Figure 4.  $\log \beta_1$  vs.  $pK_a$ . Correlation between the formation constants of Np(V)/carboxylate complexes and the  $pK_a$  of the monicarboxylic acids. (1) hydroxyacetate, (2) 2-hydroxypropanoate, (3) 2-hydroxy-2-methylpropanoate.  $I = 1.0$  M,  $t = 20 - 25^\circ\text{C}$ . Data except for gluconate are from [21].